

Comment on “Strain effect and the phase diagram of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ thin films”

Qingshan Yuan^{1,2,3}

¹*Exp VI, Center for Electronic Correlations and Magnetism, Universität Augsburg, 86135 Augsburg, Germany*

²*Texas Center for Superconductivity and Advanced Materials, University of Houston, Houston, TX 77204*

³*Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, P.R.China*

Recent experiments in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ thin films by Zhang *et al.* [Phys. Rev. B **64**, 184404 (2001)] showed that the ferromagnetic Curie temperature T_c is enhanced (reduced) by tensile (compressive) strain. The results are regarded to be anomalous because it is generally understood by the authors that the tensile strain should lead to a reduction of the electron hopping t (and thus also T_c) due to an elongation of the (in-plane) Mn-O bond length. In this comment such a general understanding of the strain effects is disapproved. It is argued that the tensile strain leads primarily to a larger Mn-O-Mn bond angle (with the Mn-O bond length nearly unchanged), thus the pure geometric consideration on t is already in the correct direction towards the experimental findings by Zhang *et al.* At the same time, an indirect strain effect under consideration of the dynamic electron-phonon coupling is proposed, which may improve the quantitative explanation.

PACS numbers: 75.70.Ak, 75.70.Gk, 71.30.+h

Very recently, the magnetic and transport properties for $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ($x = 0.05 - 0.33$) thin films grown on SrTiO_3 substrate were reported by Zhang *et al.*¹ Depending on the doping level x the films may suffer tensile ($x \leq 0.2$) or compressive ($x > 0.2$) strain. It was found that the ferromagnetic transition temperature T_c is enhanced (reduced) by the tensile (compressive) strain. The findings are regarded to be anomalous because a general understanding by the authors is “*Tensile strain elongates the in-plane Mn-O bond length d , reducing t_0 (due to $t_0 \propto d^{-3.5}$) and thus T_c ; in contrast, compressive strain raises T_c* ” (see the second paragraph in Sec. III.E). In order to explain their unusual results, Zhang *et al.* proposed a mechanism involving the orbital degree of freedom, see Ref. 2 for details. The idea is that an elongation of the in-plane Mn-O distance due to the tensile strain helps increase the $d_{x^2-y^2}$ component of the orbital state, thus in average the electron hopping would be enhanced because the hopping integral between $d_{x^2-y^2}$ orbitals is larger than that for $d_{3z^2-r^2}$ orbitals. As consistent results with theirs, Zhang *et al.* mentioned several other experimental findings: in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3/\text{SrTiO}_3$ thin films the charge ordering (CO) becomes less stable under tensile strain;³ and in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3/\text{LaAlO}_3$ thin films it is favored by compressive strain.⁴ Also, the same results as found by Zhang *et al.* in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ films were obtained by others.⁵

Although the orbital-relevant mechanism proposed by Zhang *et al.* sounds good, we disagree to their general understanding of the strain effects, and further question the reality of the proposed mechanism. In this comment, we point out that the so called general understanding, which is extensively adopted in the literature,^{1,2,5-7} is purely a *misunderstanding*. In fact, a simple correction to it, although not sufficient for a quantitative explanation, is already in the right direction toward the experimental findings by Zhang *et al.* At the same time, another mechanism in consideration of the electron-phonon

(e - p) coupling is proposed to improve the quantitative explanation. In the following mainly the tensile strain is discussed and the case for the compressive strain is the reverse.

In thin films, the tensile strain leads to an elongation of the in-plane lattice parameter a . But it does not simply signify an elongation of the (in-plane) Mn-O bond length d . A possible change of the Mn-O-Mn bond angle θ was ignored by Zhang *et al.*¹ and many others.⁵⁻⁷ There is a simple geometric relation between a and d : $a = 2d \sin(\theta/2)$. Moreover, the hopping t between two nearest neighbor Mn sites⁸ is θ -dependent itself, which reaches the maximum when $\theta = 180^\circ$. Totally, the direct dependence of t on d and θ is given by the following empirical formula:⁹

$$t \propto d^{-3.5} \sin(\theta/2). \quad (1)$$

From Eq. (1), if the angle θ is assumed independent of strain, the elongation of the lattice parameter a (and the corresponding d) will lead to a reduction of t as told by Zhang *et al.* Once it is noted that the angle θ may be modified, however, whether the hopping t (and further T_c)¹⁰ is reduced or not by the tensile strain is *not* obvious even if the length d is assumed elongated. Thus the above general understanding is *not* general at all.

Actually, there seems no direct experimental evidence that the bond length d is elongated by the tensile strain in manganite thin films. On the contrary, recent measurements in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.31, 0.39$) thin films grown on SrTiO_3 and LaAlO_3 substrates,¹¹ with extended x-ray absorption fine structure, showed that the bond length d is *fixed* at the value for the bulk materials, no matter whether the films are under tensile or compressive strain and the thickness of them. What is really modified is just the bond angle θ . It becomes larger (smaller) under the tensile (compressive) strain, being consistent with the elongation (contraction) of a . A similar result was also observed in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{LaAlO}_3$

films.¹² In addition, it was found in bulk materials $R_{1-x}A_x\text{MnO}_3$ ($R=\text{La, Pr, Nd, Y}$; $A=\text{Ca, Sr, Ba}$) with $x = 0.3, 0.33$,¹³ that changes in the average radius of the ions at (R, A) site (or equivalently the tolerance factor) only affect the mean Mn-O-Mn bond angle, with the mean Mn-O distance nearly unchanged. Based on all these findings, it is plausible to believe, for the current $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ thin films, that the primary factor modified by strain is the angle θ . Then a conclusion, which is exactly contrary to the so called general understanding, that is, the hopping t is enhanced by the tensile strain due to an enlarged θ , may be naturally obtained. In this way, the experimental findings by Zhang *et al.* are not so strange as claimed. Simultaneously, the orbital-relevant mechanism proposed by them, which is based on the hypothetical elongation of d , is not valid.

It is interesting to further make a quantitative calculation based on the above argument. When the bond length d is invariant from strain, Eq. (1) will reduce to $t \propto a$. If we assume the Curie temperature $T_c \propto t$, we have $T_c \propto a$. This means that the relative change of T_c , i.e., $\Delta T_c/T_c$ is in the same order as that of the in-plane lattice parameter a , i.e., $\Delta a/a$. In Ref. 1, for $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ ($x = 0.05$) thin films which suffer tensile strain, the *out-of-plane* lattice parameter with different film thickness h is given: 3.872\AA for $h = 85\text{nm}$ and 3.862\AA for $h = 20\text{nm}$. The relative change is calculated by $(3.862 - 3.872)/3.872 \simeq -0.3\%$. Then the corresponding relative change of a should have roughly the same magnitude but opposite sign, i.e., $\Delta a/a \simeq +0.3\%$. On the other hand, the Curie temperature T_c increases from 130K for $h = 85\text{nm}$ to 180K for $h = 20\text{nm}$, with a relative change $\Delta T_c/T_c = (180 - 130)/130 \simeq +38\%$. It is clear that the change of θ (or a) is too small to account for the significant change of T_c , although this consideration has already given the correct tendency of the T_c variation.

From the above paragraph, it has turned out that the pure geometric consideration on t as shown by Eq. (1) is not enough for a quantitative explanation of the experimental results in Ref. 1, thus other cooperative mechanisms are still required. Due to the intrinsic complexity of the concrete films, there are various factors to influence T_c such as nonstoichiometry,¹ disorder,¹⁴ phase segregation,¹⁵ etc. Here we focus on discussing the T_c variation caused by strain since the understanding of it is indispensable in thin films. Above we have addressed the direct effect due to strain on the electron hopping (and T_c). In the following we propose an indirect strain effect under consideration of the dynamic e - p coupling as a potential way to improve the quantitative explanation. Actually, since the e - p coupling is generally important in manganites, it is natural to ask the possible relevance of it to the change of T_c , as recently discussed by Chen *et al.* in $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ films.¹⁶ Explicitly, we consider that an electron at site i is coupled to a local stretching mode which involves the stretching motions at least from the in-plane oxygen ions, for example, the mode $B_{2g}(1)$ with notations in Ref. 17. The coupling is of the form:

$$f c_i^\dagger c_i Q_i, \quad (2)$$

or in boson representation ($\hbar = 1$):

$$g c_i^\dagger c_i (b_i + b_i^\dagger) \quad (3)$$

with $g = f/\sqrt{2m\omega}$. Here c_i, c_i^\dagger are fermionic operators and b_i, b_i^\dagger are bosonic operators, Q_i represents the normal coordinate describing the stretching mode considered, f, g are coupling constants, m is the oxygen mass, and ω is the normal vibration frequency. In consideration of the e - p coupling (3), the bare hopping t will be renormalized into the polaron hopping¹⁸

$$\tilde{t} \simeq t \exp[-g^2/\omega^2] = t \exp[-f^2/(2m\omega^3)] \quad (4)$$

by an extra factor. The relative change of T_c now results from that of \tilde{t} , which may become significant as shown below. To analyze the possible change of ω due to the modification of θ , we introduce the central idea proposed recently by Egami and co-workers in a different context.¹⁹ If the Mn-O-Mn bond is straight, the vibration of the middle oxygen, when compressing one Mn-O bond, will inevitably stretch the other one. On the other hand, if the Mn-O-Mn bond is sufficiently bent, the contraction of one Mn-O bond can be accommodated by unbending the Mn-O-Mn triangle, without stretching the other Mn-O bond. Therefore, in the former case, the oxygen feels stronger restoring force when it vibrates, i.e., the former case corresponds to a larger effective elastic constant K or vibration frequency ω . In our picture, the tensile strain tends to straighten the in-plane Mn-O-Mn bond, and thus will lead to a larger ω based on the above analysis. At the same time, the coupling constant f is considered to be unaffected in view of the fixed d . Then the renormalization factor will be raised. In particular, due to the exponential dependence shown in Eq. (4), a tiny hardening of ω will substantially increase the hopping \tilde{t} . Therefore, it is expected that the quantitative explanation addressed above can be largely improved. A full quantitative explanation will be left to the future when more experimental data are available, e.g., the change of ω with strain. As the first step, the experimental refinement to the local atomic configuration is needed to clarify the change of θ and/or d with strain for the specific $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ films discussed currently.

Finally, we point out that all the above ideas indicate the potential ways in which the electron itineracy can be modified by strain, thus they are of general significance for the understanding of the strain effects in manganite thin films. As mentioned above, the strain effects might not always be the dominant for experimental explanations in concrete films, nevertheless, they must be seriously studied. We mention that the (in)stability of the CO in the manganite films^{3,4} referred to in the first paragraph can be self-consistently explained by our proposal.

In summary, the so called general understanding of strain effects in manganite thin films is disapproved. It

is argued that strain primarily leads to a change of the in-plane Mn-O-Mn bond angle, thus the pure geometric consideration on the electron hopping can already give the correct tendency of the T_c variation found by Zhang *et al.* in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ thin films. Furthermore, in order to improve the quantitative explanation, an indirect strain effect under consideration of the dynamic electron-phonon coupling is proposed.

The author would like to acknowledge J. Xu, C. Schneider, T. Kopp, and R. Y. Gu for valuable discussions and J. Zhang for communications. This work was financially supported by the Deutsche Forschungsgemeinschaft through SFB 484, the National Natural Science Foundation of China (Grant No. 19904007) and the Texas Center for Superconductivity and Advanced Materials at the University of Houston.

-
- ¹ J. Zhang, H. Tanaka, T. Kanki, J. H. Choi, and T. Kawai, Phys. Rev. B **64**, 184404 (2001).
- ² T. Kanki, H. Tanaka, and T. Kawai, Phys. Rev. B **64**, 224418 (2001).
- ³ W. Prellier, A. M. Haghiri-Gosnet, B. Mercey, Ph. Lecoeur, M. Hervieu, Ch. Simon, and B. Raveau, Appl. Phys. Lett. **77**, 1023 (2000).
- ⁴ A. Biswas, M. Rajeswari, R. C. Srivastava, T. Venkatesan, R. L. Greene, Q. Lu, A. L. de Lozanne, and A. J. Millis, Phys. Rev. B **63**, 184424 (2001).
- ⁵ A. K. Pradhan, D. R. Sahu, B. K. Roul, and Y. Feng, Appl. Phys. Lett. **81**, 3597 (2002).
- ⁶ A. J. Millis, T. Darling, and A. Migliori, J. Appl. Phys. **83**, 1588 (1998).
- ⁷ G. M. Gross, R. B. Praus, S. Yaghoubzadeh, F. S. Razavi, and H. U. Habermeier, J. Alloys & Compounds **317-318**, 141 (2001).
- ⁸ In the following, the in-plane hopping is simply discussed, which contributes the dominant to the mean hopping averaged in three directions.
- ⁹ M. Medarde, J. Mesot, P. Lacorre, S. Rosenkranz, P. Fischer, and K. Gobrecht, Phys. Rev. B **52**, 9248 (1995); P. G. Radaelli, G. Iannone, M. Marezio, H. Y. Hwang, S. W. Cheong, J. D. Jorgensen, and D. N. Argyriou, *ibid.* **56**, 8265 (1997).
- ¹⁰ Due to double-exchange mechanism, a larger hopping t is favorable to the ferromagnetism, thus leading to a larger T_c .
- ¹¹ A. Miniotas, A. Vailionis, E. B. Svedberg, and U. O. Karlsson, J. Appl. Phys. **89**, 2134 (2001).
- ¹² H. L. Ju, K. M. Krishnan, and D. Lederman, J. Appl. Phys. **83**, 7073 (1998).
- ¹³ J. L. García-Muñoz, J. Fontcuberta, M. Suaaidi, and X. Obradors, J. Phys.: Condens. Matter **8**, L787 (1996); J. L. García-Muñoz, J. Fontcuberta, B. Martínez, A. Seffar, S. Piñol, and X. Obradors, Phys. Rev. B **55**, R668 (1997).
- ¹⁴ R. A. Rao, D. Lavric, T. K. Nath, C. B. Eom, L. Wu, and F. Tsui, Appl. Phys. Lett. **73**, 3294 (1998).
- ¹⁵ M. Bibes, Ll. Balcells, S. Valencia, J. Fontcuberta, M. Wojcik, E. Jedryka, and S. Nadolski, Phys. Rev. Lett. **87**, 067210 (2001).
- ¹⁶ X. J. Chen, S. Soltan, H. Zhang, and H. U. Habermeier, Phys. Rev. B **65**, 174402 (2002).
- ¹⁷ M. N. Iliev, M. V. Abrashev, H.-G. Lee, V. N. Popov, Y. Y. Sun, C. Thomsen, R. L. Meng, and C. W. Chu, Phys. Rev. B **57**, 2872 (1998).
- ¹⁸ See, e.g., Q. Yuan and T. Kopp, Phys. Rev. B **65**, 174423 (2002). In principle, there is an additional temperature-dependent factor $\coth(\omega/2T)$ in the exponential argument of Eq. (4). It is ignored if we consider a high frequency phonon mode, i.e., ω is quite a few times bigger than the temperature scale T_c [thus $\coth(\omega/2T) \simeq 1$].
- ¹⁹ T. Egami and D. Louca, J. Supercond. **13**, 247 (2000); Phys. Rev. B **65**, 094422 (2002); D. Louca, T. Egami, W. Dmowski, and J. F. Mitchell, *ibid.* **64**, R180403 (2001).